AFRL-OSR-VA-TR-2015-0166

Atomic-Scale Tuning of Layered Binary Metal OxideS

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06/01/2015
Final Report

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/ RTD
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
14-07-2015	Final Performance	01-05-2012 to 30-04-2015

4. TITLE AND SUBTITLE
Atomic-Scale Tuning of Layered Binary Metal Oxides for High Temperature Moving Assemblies

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-12-1-0221

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
ASHLIE MARTINI

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
UNIVERSITY OF CALIFORNIA MERCED
5200 N LAKE RD
MERCED, CA 95343-5001 US

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AF Office of Scientific Research
875 N. Randolph St. Room 3112
Arlington, VA 22203

10. SPONSOR/MONITOR'S ACRONYM(S)
AFOSR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
A DISTRIBUTION UNLIMITED: PB Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The objective of this research was to understand, at an atomic level, the material properties that influence the thermal, mechanical and tribological behavior of intrinsically layered binary metal oxides at high temperatures. The initial focus was silver tantalate, which is a relatively simple system that could be accurately modeled but also has significant potential as a multi-functional material for high temperature applications. Investigations were performed through a tightly integrated experimental and modeling approach in which atomistic simulations are validated by experimental observations and then fundamental mechanisms underlying the experimental observations are explained by the simulations. The following is a summary of our key accomplishments through this project that brought us from the initial work of developing experimental and simulation capabilities for studying high temperature coating materials to investigating fundamental mechanisms to explain observed friction and wear behavior and finally to using that understanding to extend the research beyond its initial focus on AgTaO3 to other materials and future materials-based coating design.

15. SUBJECT TERMS
Atomic-Scale, friction coefficient, layered structure materials, Boron Nitride, Molybdenum disulfide, tribology, oxide materials

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			ASHLIE MARTINI
U	U	U	UU		

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

				19b. TELEPHONE NUMBER *(Include area code)* (209) 228-2354

Ashlie Martini and Samir Aouadi

Grant # FA9550-12-1-0221

Final Report Submitted May 2015

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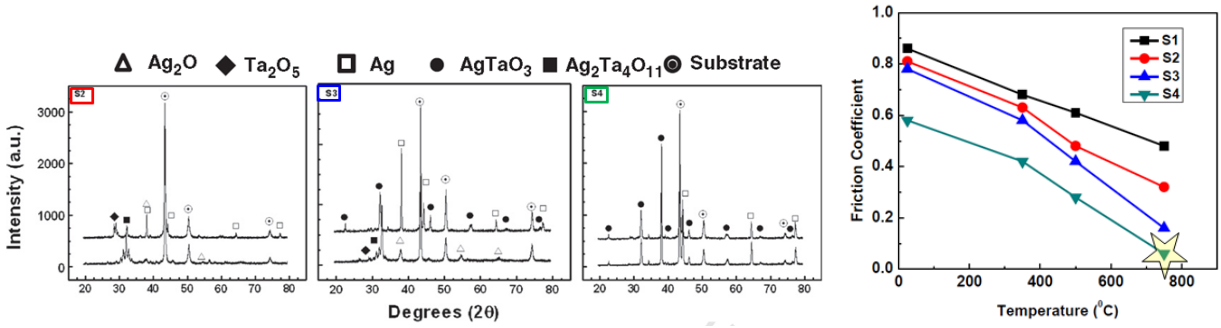
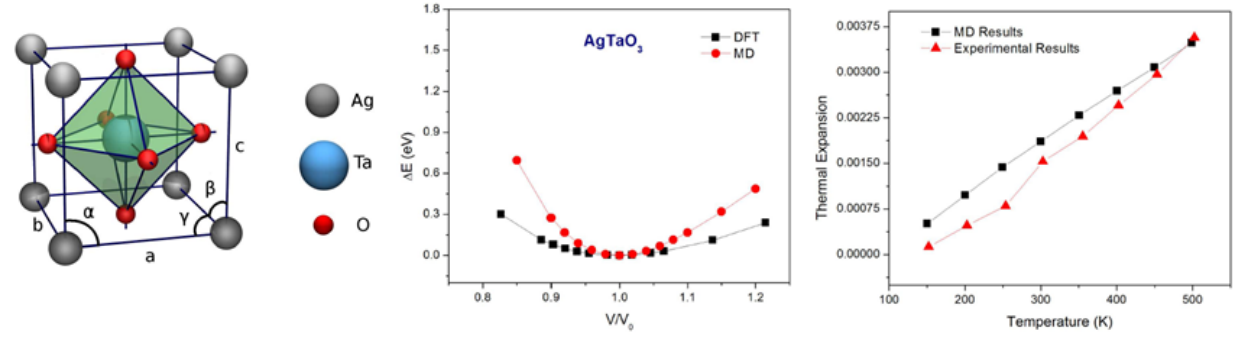
Material synthesis and characterization

We optimized the process of synthesis via magnetron sputtering to produce thermally stable silver tantalate films. X-ray diffraction confirmed the material was indeed silver tantalate and remained in that phase at high temperature. We then measured friction on these coatings from room temperature to 750 °C and observed an extremely low friction coefficient of 0.06 at 750 °C; this is the lowest friction reported at this temperature for any material to-date.



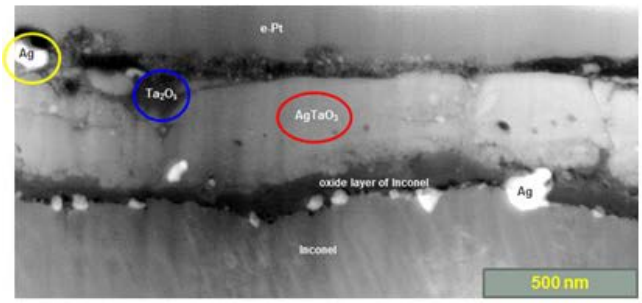
Modeling methods development

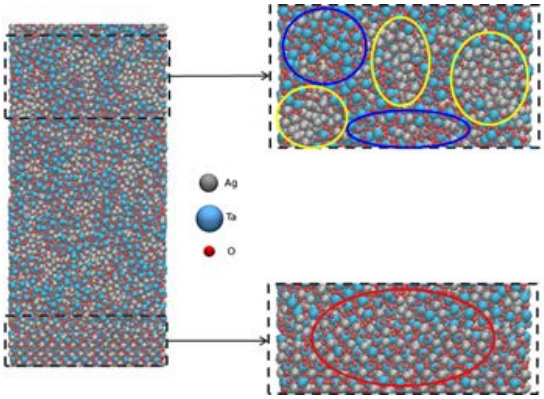
We developed an empirical model to describe the interatomic interactions in silver tantalate and validated the model's ability to reproduce structural, energetic and thermal properties of the material. Density functional theory calculations were performed to provide the energetics and previous experimental measurements were used as a reference for the structure of the material and its evolution with temperature.



Comparison of experimental and simulation results

We used the new model to perform atomistic simulations of sliding friction from room temperature to 750 °C and observed the same trend as in experiments, i.e. decreasing friction with increasing temperature where the lowest friction is observed at 750C. Results could not be quantitatively compared due to the size scale difference between the experimental (mm) and simulation (nm) contact areas. However, we analyzed the evolution in the model material during sliding and used high resolution transmission electron microscopy to characterize a cross section of the experimentally-measured material before and after sliding; both revealed segregation of the silver near the contact and the persistence of silver tantalate away from the sliding surface.



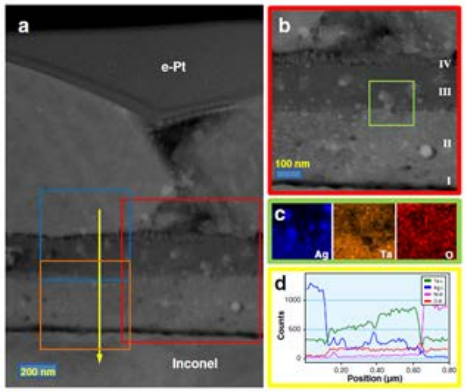


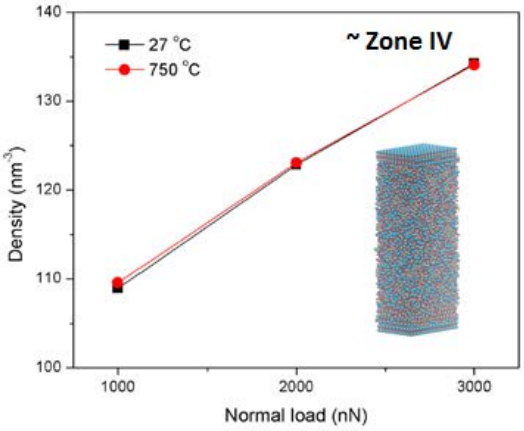
Proposed sliding mechanisms

Using the experimental measurements and observations from simulation, we identified temperature- and sliding-induced silver segregation as a key mechanism enabling low friction at high temperature. All evidence we have gathered during this project suggests that the silver tantalate acts as a reservoir continually feeding the near-surface combination of silver and tantalum oxide, where the former provides a low shear lubricious phase and the latter is very hard thereby offering reasonable wear resistance.

Exploring the effect of load

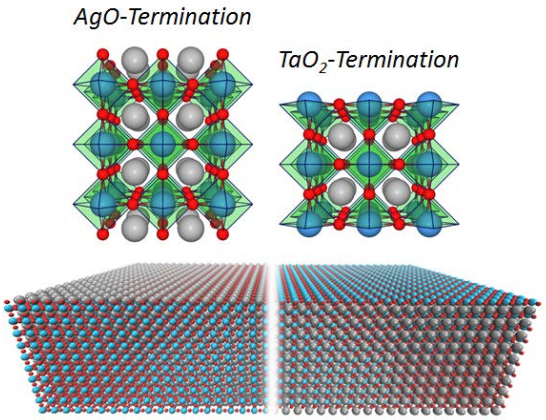
Load is well known to affect both the magnitude of friction and wear and the mechanisms by which sliding occurs on solid surface. To explore this effect for $AgTaO_3$, we characterized the load-dependence of it friction and wear at 750° using experiments and complementary simulations. These studies revealed the following: (a) friction monotonically increased with load, (b) increasing load decreased the amount of Ag on the surface of the wear track and decreased the thickness of the mechanically mixed layer that forms as a result of the reconstruction of $AgTaO_3$ into Ta_2O_5 and Ag, and (c) the silver segregation and clustering (previously shown to be directly correlated to temperature dependence of the material) can also lead to porosity in the tribofilm, and the increase of friction with load is due to the joint contributions of decreasing Ag near the surface and the associated decreased porosity of the tribofilm.

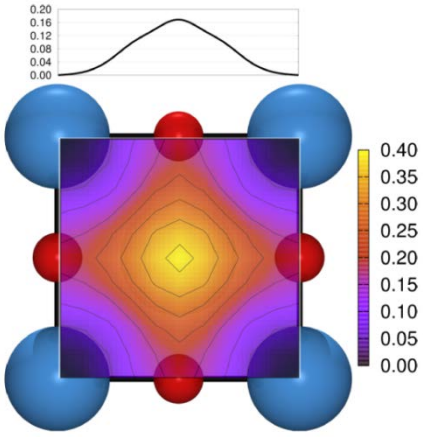




First principles-based justification of Ag-segregation mechanism

Our previous simulation and experimental results strongly suggested that Ag clustering is the key to the good performance of $AgTaO_3$ at high temperatures. We now are able to provide quantitative, atomic-scale support for this argument based combined molecular dynamics and density-functional theory simulations of surfaces and their energetics. Specifically, we showed that silver aggregation on the surface is enabled by the low energy barriers associated with silver migration. Two different surface terminations (AgO and TaO_2) were studied and we showed that the migration barrier on the AgO surface is smaller, favoring silver aggregation and ultimately giving a lower friction force. Regardless of the termination, the formation of soft silver clusters dominates the sliding behavior when enough energy (mechanical or thermal) is imparted to the surface.

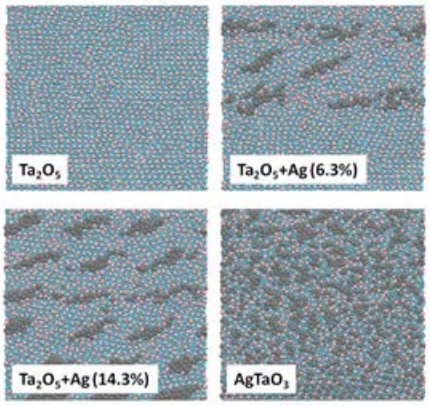


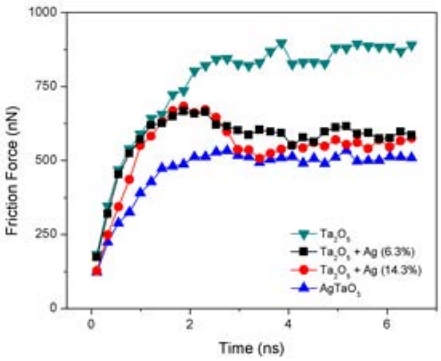


Tuning composition for optimized performance

Based on the observation that $AgTaO_3$ decomposes during sliding and the supposition that the products of this decomposition enable low friction and wear, it is possible that performance may be tuned by identifying an optimal combination of the elements in the material before sliding. To explore this possibility, we used experiments and complementary simulations to study coatings of tantalum oxide

with a small content of Ag embedded in it. Both the experimental characterization and the theoretical modeling indicated that silver migrated to the surface leaving a porous Ta_2O_5 structure underneath. In addition, this migration resulted in the formation of $AgTaO_3$ in selected regions of the coatings. The observed time-dependent surface reconstruction, which is associated with a continuous change in film structure and chemistry, resulted in a decrease in values of the friction coefficient. This study not only supports the previously-suggestion mechanisms in both Ag (soft low shear phase) and Ta_2O_5 (hard phase resisting compression) play important roles, but that the composition can in fact be tuned to modulate friction under different conditions.

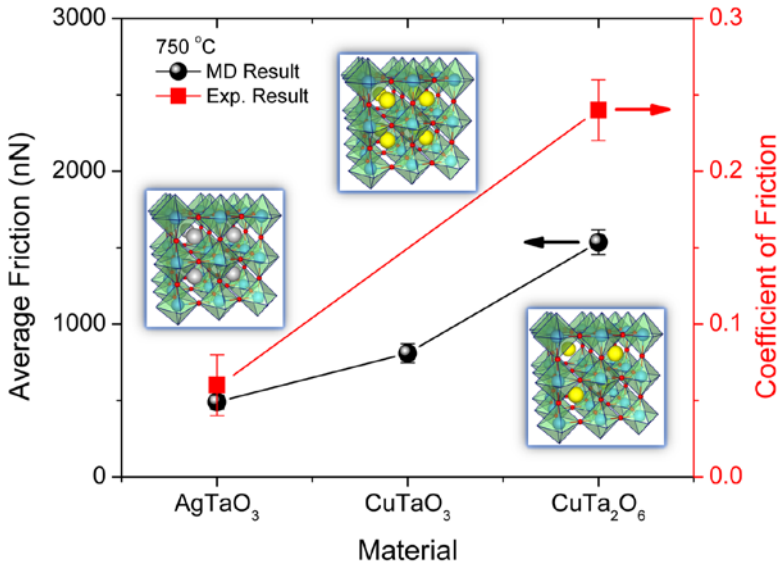




	Friction Coefficient
Ta_2O_5	0.53
Ta-O & Ag	0.14
$AgTaO_3$	0.06

Extension to other ternary oxides

Given the relatively poor wear performance of $AgTaO_3$ and the issues associated with Ag particle migration, we have been exploring alternatives to obtain both low friction and high wear resistance. We have exploring Cu-Ta-O as a potential replacement. Specifically, we used experiments, density functional theory and molecular dynamics simulation to study $CuTaO_3$ and $CuTa_2O_6$, and contrast their performance with that of $AgTaO_3$. Results show that the MD-predicted friction force follows the trend $AgTaO_3$ < $CuTaO_3$ < $CuTa_2O_6$, which is consistent with the experimentally-measured coefficients of friction. The wear performance from both MD and experiment exhibits the opposite trend, with $CuTa_2O_6$ providing the best resistance to wear. The sliding mechanisms were investigated using experimental characterization of the film composition after sliding, quantification of Ag or Cu cluster formation at the interface during the evolution of the film, and DFT energy barriers for atom migration on the material surface. All analyses support the hypothesis that the formation of metal (or metal oxide) clusters on the surface are responsible for the friction and wear behavior of these materials.


750 °C
MD Result
Exp. Result
Average Friction (nN)
Coefficient of Friction
3000
2000
1000
0
0.3
0.2
0.1
0.0
AgTaO3
CuTaO3
CuTa2O6
Material

1.

1. Report Type

Final Report

Primary Contact E-mail
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amartini@ucmerced.edu

Primary Contact Phone Number
Contact phone number if there is a problem with the report

209-228-2354

Organization / Institution name

University of California Merced

Grant/Contract Title
The full title of the funded effort.

Atomic-scale Tuning of Layered Binary Metal Oxides for High Temperature Moving Assemblies

Grant/Contract Number
AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".

FA9550-12-1-0221

Principal Investigator Name
The full name of the principal investigator on the grant or contract.

Ashlie Martini

Program Manager
The AFOSR Program Manager currently assigned to the award

Ali Sayir

Reporting Period Start Date

05/01/2012

Reporting Period End Date

04/30/2015

Abstract

The objective of this research was to understand, at an atomic level, the material properties that influence the thermal, mechanical and tribological behavior of intrinsically layered binary metal oxides at high temperatures. The initial focus was silver tantalate, which is a relatively simple system that could be accurately modeled but also has significant potential as a multi-functional material for high temperature applications. Investigations were performed through a tightly integrated experimental and modeling approach in which atomistic simulations are validated by experimental observations and then fundamental mechanisms underlying the experimental observations are explained by the simulations. The following is a summary of our key accomplishments through this project that brought us from the initial work of developing experimental and simulation capabilities for studying high temperature coating materials to investigating fundamental mechanisms to explain observed friction and wear behavior and finally to using that understanding to extend the research beyond its initial focus on $AgTaO_3$ to other materials and future materials-based coating design.

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and observed an extremely low friction coefficient of 0.06 at 750 °C; this is the lowest friction reported at this temperature for any material to-date. We then developed an empirical model to describe the interatomic interactions in silver tantalate and validated the model's ability to reproduce structural, energetic and thermal properties of the material. Density functional theory calculations were performed to provide the energetics and previous experimental measurements were used as a reference for the structure of the material and its evolution with temperature. We used the new model to perform atomistic simulations of sliding friction from room temperature to 750 °C and observed the same trend as in experiments, i.e. decreasing friction with increasing temperature where the lowest friction is observed at 750 °C. Both simulations and experiments revealed segregation of the silver near the contact and the persistence of silver tantalate away from the sliding surface. This observation suggested that low friction is possible because the silver tantalate acts as a reservoir continually feeding the near-surface combination of silver and tantalum oxide, where the former provides a low shear lubricious phase and the latter is very hard thereby offering reasonable wear resistance. Further investigation revealed that friction on AgTaO3 increases with load, and that this trend is attributable both to the silver segregation mechanisms we first identified and the associated porosity in the tribofilm. These studies were complemented by combined molecular dynamics and density-functional theory simulations of AgTaO3 surfaces (AgO and TaO2 terminated surfaces) and their energetics through which we showed showed that silver aggregation on the surface is enabled by the low energy barriers associated with silver migration. Based on the observation that AgTaO3 decomposes during sliding and the supposition that the products of this decomposition enable low friction and wear, we explored the possibility that performance may be tuned by identifying an optimal combination of the elements in the material before sliding. For this, we used experiments and complementary simulations to study coatings of tantalum oxide with a small content of Ag embedded in it. Both the experimental characterization and the theoretical modeling indicated that silver migrated to the surface leaving a porous Ta2O5 structure underneath. In addition, this migration resulted in the formation of AgTaO3 in selected regions of the coatings. The last major research focus of this project was extension to other materials, motivated by the relatively poor wear performance of AgTaO3 and issues associated with Ag particle migration in components. Specifically, we studied Cu-Ta-O compounds and contrasted their performance with that of AgTaO3. Simulations and experiments showed that friction force follows the trend AgTaO3 < CuTaO3 < CuTa2O6. However, the wear performance was found exhibits the opposite trend, with CuTa2O6 providing the best resistance to wear. The sliding mechanisms were investigated using experimental characterization of the film composition after sliding, quantification of Ag or Cu cluster formation at the interface during the evolution of the film, and DFT energy barriers for atom migration on the material surface. All analyses supported the hypothesis that the formation of metal (or metal oxide) clusters on the surface are responsible for the friction and wear behavior of these materials.

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Archival Publications (published) during reporting period:

Gao H, Otero-de-la-Roza A, Gu J, Stone DS, Aouadi SM, Johnson ER and Martini A, "(Ag,Cu)-Ta-O ternaries as high temperature solid lubricants", ACS Applied Materials & Interfaces, Under Review

Stone DS, Gao H, Chantharangsi C, Paksunchai C, Bischof M, Martini A and Aouadi SM (2014) "Reconstruction mechanisms of tantalum oxide coatings with low concentrations of silver for high temperature tribological applications", Applied Physics Letters, 105, 191607.

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Goa H, Otero-de-la-Roza A, Aouadi SM, Martini A and Johnson ER (2014) "Chemical Basis of the Tribological Properties of AgTaO3 Crystal Surfaces", Journal of Physical Chemistry C, 118, 012125.

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Dong Y, Li Q and Martini A (2013) "Molecular dynamics simulation of atomic friction: A review and guide", Journal of Vacuum Science and Technology A, 31, 030801.

Gao H, Otero-de-la-Roza A, Aouadi SM, Johnson ER and Martini A (2013) "An Empirical Model for Silver Tantalate", Modelling and Simulation in Materials Science and Engineering, 21, 055002.

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D.S. Stone, S. Harbin, H. Mohseni, J.-E. Mogonye, T.W. Scharf, C. Muratore, A.A. Voevodin, A. Martini and S.M. Aouadi (2013) "Lubricious silver tantalate films for extreme temperature applications", Surface and Coatings Technology, 217, 140.

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Dong Y, Perez D, Gao H and Martini A (2012) "Thermal activation in atomic friction: revisiting the theoretical analysis", Journal of Physics: Condensed Matter, 24, 265001.

Changes in research objectives (if any):

N/A

Change in AFOSR Program Manager, if any:

N/A

Extensions granted or milestones slipped, if any:

N/A

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

	Starting FY	FY+1	FY+2
Salary			
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Report Document

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